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Coherent vibration and ultrafast dynamics upon bond formation in excited dimers of Au(I) complex

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Au-Au bond strengthening in photoexcited dimers of Au(I) complex is captured in solution as oscillations of femtosecond absorption signals. The subsequent dynamics, when compared to the trimer's data, confirm that the bent-to-linear structural change of the trimer occurs at early picoseconds.

The Molecule reacts by forming and/or breaking the chemical bonds to be converted to the product, which eventually alters the material properties. In this sense, the change in the chemical bonds is one of the most important elementary events in chemistry not only for synthesis but also for understanding various phenomena from the microscopic viewpoints. Therefore, observing the moment of the bond formation/breaking discloses the essence of chemical reactions and stimulates our fundamental interests. Such a bond rearrangement itself is primarily electronic in nature and proceeds within extremely short times, which makes the real-time observation yet challenging.[1] However, the associated nuclear rearrangement, e.g. changes in the bond length and angle, would occur on the femtosecond time scale that is accessible with advanced ultrafast vibrational spectroscopy.[2-7]

Oligomers of a simple Au(I) complex, dicyanoaurate ($[Au(CN)_2^-]$), provide a unique opportunity to investigate the photo-induced bond formation and associated structural change, which are induced by the intermolecular aurophilic interaction.[8, 9] Due to weak aurophilic attractive interaction (~0.1 eV) in the ground state,[10] the complex self-assembles in water and forms a loosely-bound dimer, trimer (and even larger oligomers), depending on the concentration. With ultraviolet irradiation, an electron in the $d_{z2}\sigma^*$ antibonding orbital is excited to the $p_z\sigma$ bonding orbital between the Au atoms, which strengthens the Au-Au bond (~1 eV). As a result, the excited oligomer with tight Au-Au covalent bond(s) is generated (Figure 1). Emission from the excited oligomer varies in color depending on the size, which attracts much interest in photochemistry of Au(I) complexes.[11-18]

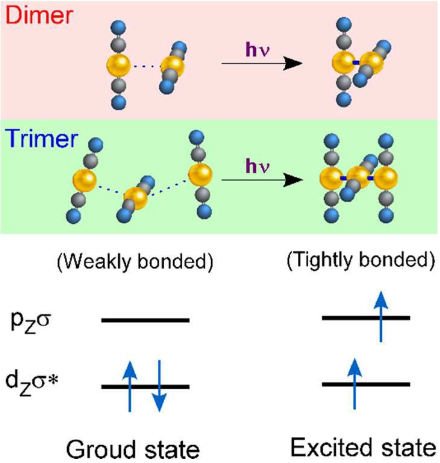

Figure 1. The frontier orbitals involved in photoexcitation of the $[Au(CN)_2^-]$ dimer and trimer. With photoexcitation, the oligomers with a weakly bonded structure in the ground state are transformed into the oligomer having a tightly bonded, linear staggered structure.

Ultrafast dynamics of the $[Au(CN)_2^-]$ oligomer associated with the bond formation was first studied by femtosecond absorption spectroscopy with selective excitation of the trimer at 310 nm in water.[5] The observed excited-state absorption around 600 nm exhibited temporal oscillations in initial few picoseconds, which reflects coherent stretching motions of the Au–Au bonds (66 and 87 cm^{-1}). This coherent motion is caused by a distinct difference in the equilibrium Au-Au distances between the ground and excited states, and hence this observation directly manifests a rapid contraction of the Au-Au bond with electronic excitation. In addition, the 600-nm transient band subsequently exhibited a 2.1-ps rise. This 2.1-

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Electronic Supplementary Information (ESI) available: [Experimental procedures; Absorption spectra; Steady-state and time-resolved emission spectra; Global fitting analysis of the femtosecond time-resolved absorption signals; Femtosecond time-resolved absorption data of 0.075 mol/dm^3 solution; Optimized structure of $[Au(CN)_2^-]_n$ in the T_1 state.]. See DOI: 10.1039/x0xx00000x ps dynamics was assigned to a change in the Au-Au-Au angle based on time-dependent density functional theory (TDDFT) calculations which showed that the absorption intensity at 600 nm sensitively changes with the bending angle. Thus, femtosecond absorption spectroscopy of the trimer concluded the abrupt contraction of the Au-Au bond upon electronic excitation and subsequent slower structural change (2.1 ps) from a loosely-bent to the rigid linear structure.

Very recently, a femtosecond X-ray scattering experiment was performed for $[Au(CN)_2^-]$ aqueous solution with optical excitation at 267 nm.[19] With the obtained radial distribution profiles, it was claimed that the ground-state trimer possessing a loose bent geometry rapidly transforms into the tight linear geometry within a few hundred femtoseconds after photoexcitation, which is followed by a slow (1.6 ps) further contraction of the Au-Au bonds. Therefore, although both the femtosecond optical and X-ray experiments have been performed for elucidating rapid Au-Au contraction due to tight covalent bond formation in the $[Au(CN)_2^-]$ trimer, the conclusions about the time scale of the associated structural change are distinctly different.[20] In other words, the ~2-ps dynamics commonly observed in both experiments was assigned to the bent-to-linear structural change in the optical spectroscopy while it is attributed to the additional contraction of the Au-Au bond in the X-ray study.

To resolve this controversy and obtain a coherent view about the tight Au-Au bond formation of $[Au(CN)_2^-]$ oligomers, it is essential to examine the dynamics of the dimer, and compare it with the dynamics of the trimer. This is because the bent-to-linear structural change only occurs in the trimer but not in the dimer, which unambiguously identifies the relevant dynamics experimentally. In fact, lack of information on the excited-state dynamics of the dimer prevents us from obtaining a coherent view for the excited-state dynamics of the $[Au(CN)_2^-]_n$ oligomers because the dimer is the simplest, and coexists with any kind of other $[Au(CN)_2^-]_n$ (n>2) oligomers in solutions. Herein, we present steady-state and ultrafast absorption/fluorescence studies of the $[Au(CN)_2^-]_2$ dimer in aqueous solution. The present study shows that selective excitation of each oligomer is critical for resolving the controversy, and the comparison of the results for the dimer and trimer clarifies that the bent-to-linear structural change proceeds in early picoseconds.

In aqueous solution of $[Au(CN)_2^-]$, the monomer, dimer, and even larger oligomers can exist due to association in the ground state through the aurophilic interaction, so that selective excitation of the dimer is not trivial. Steady-state absorption of a dilute solution (e.g., $C = 10^{-4}$ mol/dm^3) shows that the monomer absorbs only at wavelengths below 245 nm.[21] As the concentration increases, the absorption band extends to the red and exhibits a shoulder due to the dimer in the 250 – 280 nm region. Concentration dependence of the absorbance at 266 nm revealed that a simple monomer – dimer equilibrium holds for the range of 0 - 0.04 mol/dm^3, indicating that the contribution of larger oligomers is very minor at $C < 0.04$ mol/dm^3. Therefore, the excitation of ~0.04 mol/dm^3 solution at ~270 nm, where the monomer does not show any absorption, realizes a situation that the dimer is most predominantly excited (see ESI, section 2 for details). In fact, steady-state emission taken under this condition showed the dimer (330 nm) and trimer (400 nm) bands with a relative band area of 1 : 4.5. Considering that the emission lifetimes of the dimer and trimer are 25 ps and 1.6 ns, respectively (see ESI, section 3 for details), the initial population ratio of the photoexcited dimer and trimer is evaluated as $N_2^0 : N_3^0 = 93 : 7$ assuming that the radiative rate constants are not so different between dimers and trimers.

Ultrafast dynamics of the excited dimer was examined by femtosecond time-resolved absorption measurements for a 0.038 mol/dm^3 aqueous solution of $[Au(CN)_2^-]$ with excitation at 270 nm (Figure 2). Upon photoexcitation, transient absorption immediately appears at ~400 nm, which is followed by a rapid growth of a transient band at 550 nm until ~1 ps (Figure 2a). Then the 550-nm band decays from 1 ps to 100 ps, leaving a slightly red-shifted band at 560 nm (Figure 2b). The 560-nm band further decays on a much longer time scale up to the maximum time delay of our measurement (800 ps, Figure 2c). A global fitting analysis in the 400-710 nm region showed that the temporal profile at 550 nm is well reproduced by a tri-exponential function with time constants of 0.2 ps, 26 ps, and ~ 1 ns (Figure 2d, and see Figure S6 in ESI for detail). They correspond to the initial rise of the 550-nm band, its subsequent decay, and the slow decay of the 560-nm band.

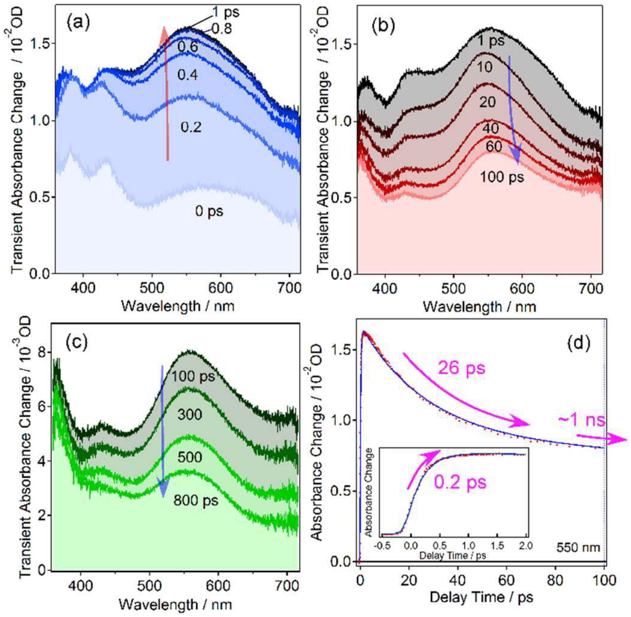

Figure 2. Femtosecond time-resolved absorption spectra of $K[Au(CN)_2]$ in aqueous solution: (a) 0–1 ps and (b) 1–100 ps (c) 100-800 ps (0.038 mol/dm^3, $\lambda_{ex} = 270$ nm). (d) Temporal trace of the transient absorption signal at 550 nm in the time region of −5–100 ps (inset: −0.5–2 ps).

Since the initial transient absorption at around 400 nm is observed immediately with photoexcitation, it is assignable to the photogenerated S_1 state of the dimer. The subsequent 0.2-ps rise that is evident in the 450-700 nm region is similar to the transient absorption change due to the intersystem crossing observed for the trimer in the previous study[5]: In the case of the trimer, a transient absorption band at 590 nm grows up as the T_1 state appears with a 0.24-ps time constant. From the similarity of the peak wavelength of the transient band as well as its rise time, the 550-nm transient band observed in the present study is assigned to the T_1 state of the dimer. Namely, as the S_1 state of the dimer is converted to the T_1 state by the intersystem crossing, the T_1 absorption grows up at around 550 nm with the 0.2-ps time constant. Then, the 550-nm band decays with the time constant of 26 ps. This time constant is essentially the same as the phosphorescence lifetime of the dimer measured by the TCSPC method (25 ps, Figure S4b), which confirms that the transient band at 550 nm is due to the T_1 state of the dimer. After disappearance of the T_1 state of the dimer, we observed the transient band at 560 nm that decays with ~ 1 ns time constant. This 560-nm band is not due to the dimer but is assignable to the T_1 state of the trimer that coexists in the solution, because the decay time constant accords with the phosphorescence lifetime of the trimer (1.6 ns, Figure S4c). The temporal profile at 550 nm (Figure 2d) as well as analysis for species associated spectra (Figure S7) show that the T_1 state of the trimer, despite its small initial population (N_3^0 = 7 %), has a comparable absorption intensity to that of the T_1 dimer. This suggests that the oscillator strength of the T_1 absorption of the $[Au(CN)_2^-]$ trimer is much larger than that of the dimer. This tendency was reproduced in our TDDFT calculations, which gives the oscillator strengths of $f_{\mathrm{dimer}} = 0.3$ and $f_{\mathrm{trimer}} = 0.7$ for the T_1 dimer and trimer, respectively,[5] although quantitative comparison between the experimental data and theoretical calculation is still difficult for the transition intensity of excited-state metal complexes. We also note a transient absorption feature below 400 nm evolves during deactivation of the T_1 dimer (1 – 100 ps) and remains unchanged until 800 ps. At present, the assignment of this long-lived spectral feature is not clear, but it may be due to a transient (ground-state) product.

A conspicuous feature of the present femtosecond absorption data is that we observed coherent nuclear motions of the excited dimer in initial few picoseconds. In Figure 3a, the time-resolved signals at two wavelengths (533 nm and 559 nm) are shown after the population component (calculated with the 0.2-ps, 26-ps, and 1-ns time constants) is subtracted from each time-resolved trace. They clearly show common oscillatory features. Since the probe pulse monitors the excited-state absorption of the dimer but it does not spectrally overlap with the ground-state absorption, these oscillations are attributable to the coherent nuclear motions of the excited dimer. The observation of the coherent nuclear motions is an important feature of ultrafast spectroscopy, because the pump pulse not only generates the excited-state population but also creates vibrational coherence if the pump duration is shorter than the vibrational period.[4]

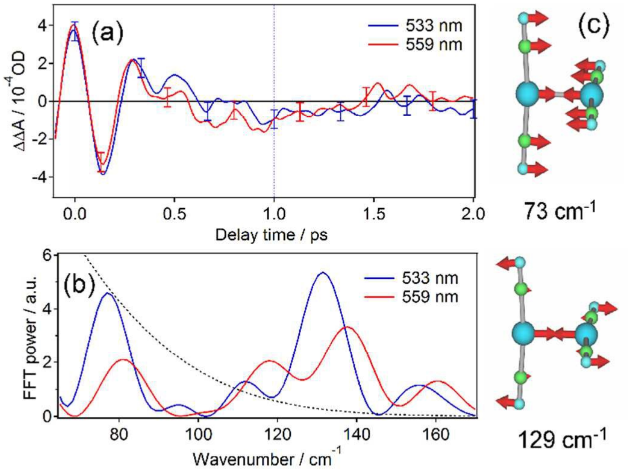

Figure 3. (a) Oscillatory components extracted from the time-resolved absorption signals at 533 nm (average over the 519-546 nm region) and 559 nm (546-572 nm). (b) Fourier transform power spectra of the oscillatory components. The broken curve shows the sensitivity in the frequency domain that was calculated from the Gaussian instrumental response function with a full width at half maximum of 0.2 ps. (c) Nuclear motions of the two Au–Au stretch modes calculated for the T_1 state of the dimer.

Figure 3b depicts the Fourier transform power spectra of the oscillatory components observed at the two selected wavelengths. They exhibit a distinct two features at around 80 cm^{-1} and around 130 cm^{-1}. Density-functional theory calculations for the T_1 dimer showed that there are only two totally symmetric modes below 200 cm^{-1}, as depicted in Figure 3c. The calculated frequencies, 73 cm^{-1} and 129 cm^{-1}, coincide very well with the peak frequencies found in the Fourier transform. Because vibrational coherence of the totally symmetric mode is induced by ultrashort excitation in ordinary cases, the observed two coherent vibrations are assigned to these two modes of the dimer. We note that the frequencies observed for the T_1 dimer (80 and 130 cm^{-1}) are significantly different from those observed for the T_1 trimer (66 and 87 cm^{-1}). In particular, the absence of any noticeable features around the frequencies of the T_1 trimer in Figure 3b indicates that the contribution of the coexisting minor trimer to the oscillatory component is negligible when the sample is excited at 270 nm. As shown in Figure 3c, the two coherent motions observed for the dimer contain significant contributions of the Au–Au stretch (or contraction) motion. This manifests that the equilibrium Au–Au bond length is largely different between the ground and excited states of the dimer, and the tight Au–Au bond is formed immediately after photoexcitation with significant contraction of the Au–Au bond length.

It is remarkable that the time-resolved absorption signal of the dimer in early picoseconds is distinctly different from that of the trimer.[5] As shown in Figure 2d, the dimer exhibits the 0.2-ps rise of the T_1 absorption and the subsequent 26-ps decay. The trimer also showed the 0.24-ps rise of the T_1 absorption, but it exhibited a further substantial 2.1-ps rise before the deactivation of the T_1 state which occurs on the nanosecond time scale.[5] This 2.1-ps dynamics of the T_1 trimer was assigned to the structural change from loose bent structures to the linear staggered structure. Because such a structural change in the Au–Au–Au angle does not exist in the dimer, it is very natural that the 2.1-ps dynamics is not observed for the dimer. The lack of the 2.1-ps dynamics in the data of the dimer confirms its assignment to the structural change involving the bending degree of freedom which is lacking in the dimer. It is worth noting that the 2.1-ps dynamics comes to appear in a slightly higher-concentration solution (0.075 mol/dm^3, Figure S8), where the initial population ratio of the photogenerated trimer becomes larger.

In the recent femtosecond X-ray study on the tight Au–Au bond formation of the $[Au(CN)_2^-]$ trimer, it was claimed that the contraction of the Au-Au bond and associated conformational change from loose bent structures to the rigid linear structure take place within a few hundred femtoseconds after photoexcitation, which is followed by a gradual, further contraction of the Au–Au bond in early picoseconds (1.6 ps). This picture is distinctly different from the results of our previous study on the trimer, which concluded that the Au–Au bond is contracted soon after photoexcitation, followed by the bent-to-linear conformational change with a time constant of 2.1 ps. In our previous study, we photoexcited a concentrated solution (0.28 mol/dm^3) at 310 nm, where the dimer as well as the monomer does not show any absorption. This assured that the trimer was selectively photoexcited in the experiment. In contrast, the femtosecond X-ray experiment was carried out for a 0.3 mol/dm^3 aqueous solution with optical excitation at 267 nm. In this case, the 267-nm light can excite both the dimer and trimer that coexist in the sample solution, and a mixture of the photoexcited dimer and trimer is supposed to be probed by the X-ray scattering. They showed that no difference was found between transient X-ray data measured at 100 ps with excitation at 267 nm and 310 nm, as an evidence to claim that X-ray scattering obtained with 267-nm excitation exclusively monitors the excited trimer. However, as clearly shown in the present study, the lifetime of the excited dimer is as short as 26 ps, and hence it no longer exists at 100 ps. In other words, even when both the dimer and trimer are photoexcited simultaneously, only the excited trimer can be observed at 100 ps. Thus, the comparison of the transient X-ray data at 100 ps cannot be an evidence that the trimer is predominantly photoexcited at 267 nm and is probed by the X-ray scattering. Because the X-ray probes all the species contained in the sample solution without species selectivity, the reported time-resolved X-ray scattering highly likely monitored the structural dynamics of a mixture of the photoexcited dimer and trimer, from which it is difficult to extract the bond formation dynamics of each oligomer.

In the present study, the photo-induced dynamics due to the $[Au(CN)_2^-]$ dimer was clarified with femtosecond time-resolved absorption, by carefully choosing the photoexcitation condition. The observed time-resolved absorption dynamics of the dimer is compared with that of the trimer, which provides a consistent view on the structural changes and their time scales of the $[Au(CN)_2^-]$ oligomers, as summarized in Figure 4. The dimer in the ground state is formed with a loose Au-Au bond due to the weak intermolecular aurophilic interaction.[21] Upon photoexcitation, the change in the electronic configuration strengthens the Au-Au bond immediately, thereby forming the dimer with a tight covalent bond.[8] The rapid contraction of the Au-Au distance induces the Au-Au stretch coherent nuclear motions, which are observed as the oscillation of the time-resolved absorption signal of the T_1 state (80 and 130 cm^{-1}). The excited dimer undergoes intersystem crossing with the 0.2-ps time constant, and then the resultant T_1 state disappears with the 26-ps lifetime. On the other hand, the trimer in the ground state has a weakly-bound, bent structure formed with loose Au-Au bonds.[5] As in the case of the dimer, the trimer undergoes rapid contraction of the Au-Au bonds immediately after photoexcitation, which induces coherent Au-Au stretch vibrations (66 and 87 cm^{-1}). This coherent motion also gives rise to the oscillation of the T_1 absorption that appears with ~0.3-ps intersystem crossing. Differently in the trimer, the T_1 state subsequently transforms its conformation from the initial bent structure to the linear staggered structure with the 2.1-ps time constant, which is observed as the gradual growth of the transient absorption. This change in the Au-Au-Au angle only occurs in the trimer, so that the corresponding dynamics is not observed in the dimer. Finally, the excited trimer decays with a time constant as long as ~2 ns.

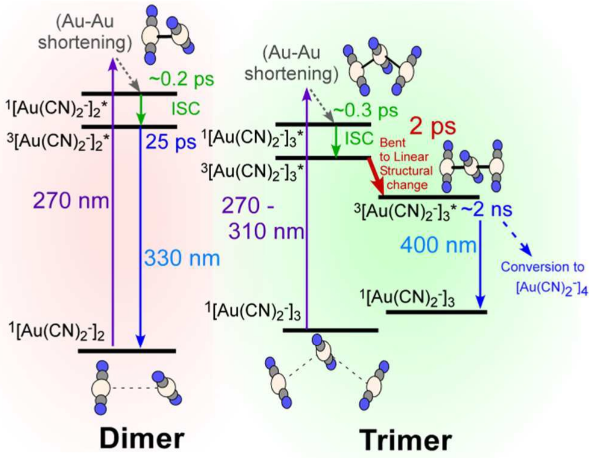

Figure 4. Schematic illustration of the relaxation pathways and relevant structural changes for excited-state $[Au(CN)_2^-]_2$ and $[Au(CN)_2^-]_3$ in aqueous solution

Ultrafast spectroscopy of the selectively-excited $[Au(CN)_2^-]$ oligomers clarifies the elementary events and their time scales associated with the bond formation. The present result obtained from the Au(I) complex provides deep insights into the reaction dynamics and relevant structural changes in metallophilic systems.

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Synopsis for TOC

Au-Au bond strengthening in photoexcited dimers of Au(I) complex is captured in solution as oscillations of femtosecond absorption signals.